



King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



REVIEW

Photochemical studies: Chromones, bischromones and anthraquinone derivatives



Mohamad Yusuf ^{*}, Indu Solanki, Payal Jain, Rupesh Kumar

Department of Chemistry, Punjabi University, Patiala 147002, Punjab, India

Received 7 September 2013; accepted 16 November 2014

Available online 25 November 2014

KEYWORDS

Chromones;
Bischromones;
1,4-Biradical;
Photochemical H-abstraction;
Photocyclization;
Anthraquinones

Abstract Photochemical reaction is a chemical reaction initiated by the absorption of energy in the form of light resulting in different types of reaction. Chromones, bischromones and anthraquinones are the bichromophoric molecules which contain the carbonyl group and double bond in conjugation. Photochemical reactions of these compounds result in the formation of such molecules which are not obtained via conventional methods. This review article describes the photochemical transformations of chromones, bischromones and anthraquinone derivatives and here main emphasis has been laid upon the intramolecular photochemical H-abstraction reactions that provide many exotic heterocyclics as the final photoproducts.

© 2014 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Contents

1. Introduction	1198
2. Phototransformation in chromones	1199
2.1. Photodimerization	1199
2.1.1. Intermolecular dimerization	1199
2.1.2. Intramolecular dimerization	1200
2.2. Photo-dehalogenation	1200
2.3. Photochemical oxidation	1200
2.4. Photochemical ring contraction	1200
2.5. Photochemical H-abstraction	1200
2.5.1. Synthesis of tetracyclic products	1200

* Corresponding author.

E-mail address: yusuf_sah04@yahoo.co.in (M. Yusuf).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

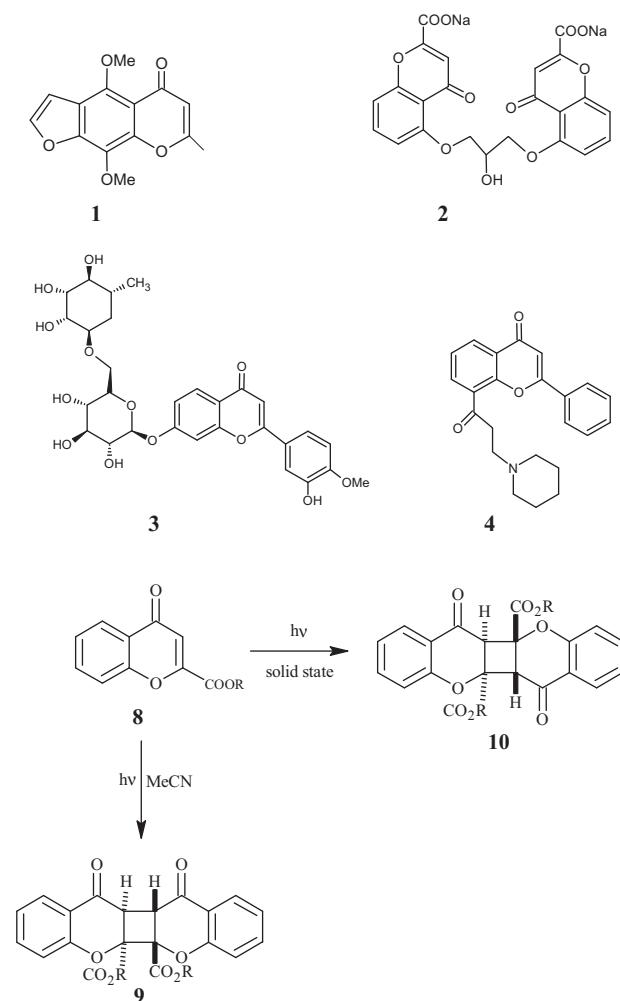
2.5.2. Synthesis of spiropyrans	1205
2.5.3. Synthesis of vinyl ethers	1205
3. Photochemical H-abstraction in bischromones	1205
3.1. Photocyclization reaction	1206
3.2. Photoisomerization	1207
4. Photochemical reactions of anthraquinones	1208
4.1. Photo-oxidation	1209
4.2. Photochemical H-abstraction	1209
4.2.1. Synthesis of α,β -unsaturated aldehyde	1209
4.2.2. Synthesis of 1-hydroxy-9,10-anthraquinones	1209
4.2.3. Synthesis of 3-alkynals	1210
4.3. Photochemical cyclization	1210
4.4. Laser flash photolysis	1210
5. Conclusion	1210
Acknowledgement	1210
References	1210

1. Introduction

Photochemical reaction (Michl and Koutecky, 1990; Coxon and Halton, 1987; Scaino and Johnston 1989; Margaretha, 1982; Horspool and Song, 1995; Neckers, 2008; Boyd and Zopp, 2004) is a chemical reaction initiated by the absorption of energy in the form of light resulting in the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules. A molecule in its ground state can absorb a quantum of light energy or photon and go to a higher-energy state, or excited state. Thus, photo-excited molecules are more reactive than ground-state molecules and can undergo entirely different reactions than the more stable molecule and lead to several reaction pathways. A part of the molecule that is responsible for the absorption of light is called chromophore. Carbonyl compounds undergo mainly two types of reactions: Norrish type I (α -cleavage) and Norrish type II (γ -H abstraction). α -Cleavage is followed by recombination, intermolecular H-abstraction or loss of CO to give various photoproducts (Coyle and Carless, 1972; Pitts and Wan, 1966; Coyle, 1985; Chapman and Weiss, 1973; Jockusch et al., 2001; Eichler et al., 1980a,b). γ -H abstraction is mainly found in α,β -unsaturated carbonyl compounds which lead to the formation of 1,4-biradical which either undergo (a) Reverse hydrogen transfer (b) α,β cleavage or (c) Radical recombination i.e. Yang cyclization (Yang and Yang, 1958).

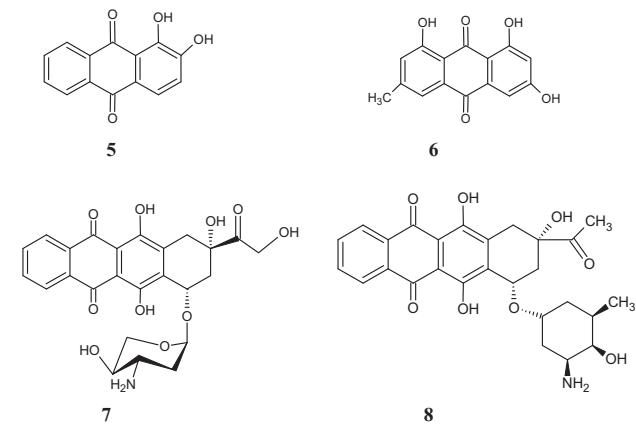
Chromones and bischromones are the very important class of heterocyclic compounds which contain two chromophoric units i.e. C=C and C=O. They are also found to be associated with a large number of biological as well as pharmacological activities. The various activities associated with chromones include antioxidant (Gomes et al., 2009; Shanti et al., 2013; Phosrihong et al., 2012), anti-inflammatory (Khadem and Marles, 2012; Deshmukh et al., 2009), antiulcer (Lemos et al., 2012), biocidal (Sharma et al., 2011), wound healing (Hajhashemi et al., 2012), immune stimulatory, (Gamal-Eldeen et al., 2007) etc. Khelin **1** was the first chromone extracted from *Anmi visnaga*, used as a diuretic to relieve renal colic (Edwards and Howell, 2000), as a smooth muscle relaxant (Nordlund, 2006) and in the treatment of vitiligo, a pigmentation disorder (De Leeuw et al., 2011). Other chromone derivatives for example sodium cromoglycate **2**, diosmin **3** and flavoxate **4** are used as a mast cell stabilizer in allergic

asthma and allergic conjunctivitis, for the treatment of various diseases and as a smooth muscle relaxant to treat urge incontinence (Holgate and Polosa, 2008; Frick, 2000; Ruffmann, 1988). These pharmacological properties have been the major incentive behind the synthesis of chromones which are obtained via different routes.

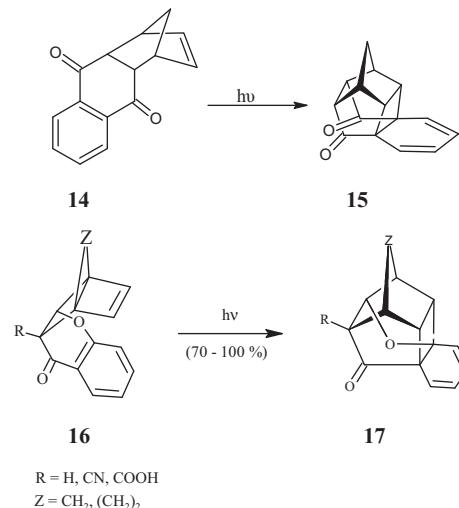


Scheme 1 Intermolecular dimerization.

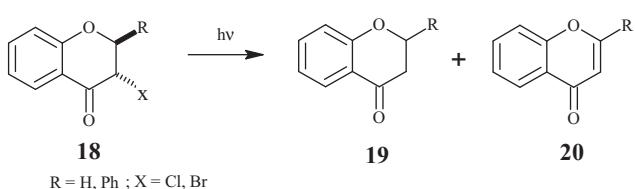
Anthraquinones are another class of compounds which contain conjugated cyclic diketone moiety. These substrates are aromatic that are present everywhere as natural pigment and anthracyclines, a large class of antibiotic molecules which are involved in electron transport system. Alizarin **5** is a well known dye which was initially isolated from the roots of *Rubia cordifolia* plants. Emodine **6** is an anthraquinone derivative responsible for the red color of *Rheum rhabarbarum* (rhubarb) plants. Epirubicine **7** and idarubicine **8** are the examples of anthracycline antibiotics produced by *Streptomyces* bacteria (Weiss, 2010).



Chromones upon exposure to light undergo various transformations such as photocycloaddition, photodimerization, photoisomerization, phototautomerization, photorearrangements, photo-oxidation and photoreduction reactions whereas anthraquinones mainly undergo photoreduction, photo-oxidation and photocyclization. Out of these photoreactions, H-abstractions have been significantly utilized in the past for the preparation of new heterocyclics. The photochemistry of chromones has been extensively studied and lots of efforts are still going on. Alkoxychromones upon photoirradiation undergo -H abstraction through the photochemically excited carbonyl group which give 1,4-biradicals. The cyclization reaction of intermediate biradical with the 2-aryl ring gives many unique tetracyclic pyran derivatives. The linking of two chromone moieties with the help of a carbon chain provides bischromones and these molecules also suffer intramolecular H-abstraction to generate a variety of heterocyclic substrates. Alkoxyanthraquinones under the influence of light either undergo δ -H abstraction by the photoexcited carbonyl group or electron transfer from oxygen to the carbonyl group to give negative charge on carbonyl oxygen resulting in the formation of biradical leading further to a number of reactions. Hence, photochemical reactions of chromones, bischromones and



Scheme 3 Intramolecular dimerization.



Scheme 4 Photo-dehalogenation.

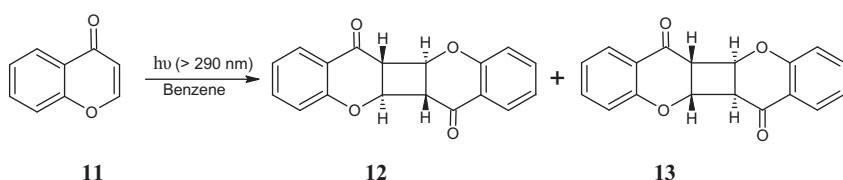
anthraquinone derivatives have attracted the attention of the synthetic organic chemists and these reactions are discussed in brief in this review article. In the recent years, some review articles have been published upon the photochemical reactions (Hoffmann, 2008) of chromones (Kumar and Yusuf, 2006), flavonoids (Sisa et al., 2010) and N-alkyl/N-aryl substituted phthalimides (Horvat et al., 2010).

2. Phototransformation in chromones

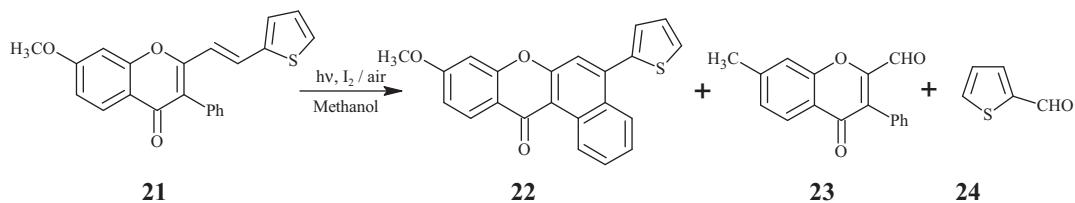
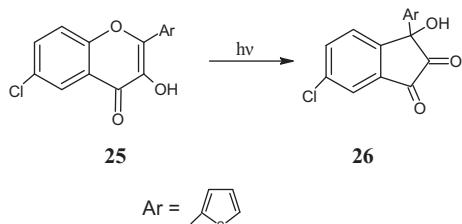
2.1. Photodimerization

2.1.1. Intermolecular dimerization

Masami Sakamoto et al. (2010) described two examples of photodimerization of chromane derivatives in solution and solid state (Scheme 1). The irradiation of chromone-2-carboxylic esters **8** in solution phase resulted in the stereo- and regio-selective formation of C₂ chiral anti-HH dimer **9** which is realized from the triplet excited state. On the contrary, photolysis in the solid state provided anti-HT dimer **10** which is exclusively controlled by the molecular arrangement in the crystal.



Scheme 2 Intermolecular photoreactions.

**Scheme 5** Photochemical oxidation.**Scheme 6** Photochemical ring contraction.

The photoirradiation of the chromone **11** led to the formation of two types of dimers, *anti*-HT **12** (head-to-tail) and *trans*-fused HT **13** isomers (Sakamoto et al., 2009), whose structures were established with the help of X-ray structural analysis (Scheme 2).

2.1.2. Intramolecular dimerization

The Diels–Alder adducts of chromones (Valiulin and Kutateladze, 2010) are reported to undergo an intramolecular [2 π + 2 π] alkene–arene photocyclization (Scheme 3), leading to a versatile polycyclic diene **14** and **16**, which are further capable of dimerization to give **15** and **17** or can be introduced into a high yield photoprotolytic oxametathetic sequence.

2.2. Photo-dehalogenation

In another significant work, Delgado et al. (2007) have studied the photolysis of 3-halo-2,3-dihydrobenzopyran-4-ones **18** in acetonitrile and hexane that yielded dehalogenated dihydrobenzopyran-4-ones **19** and benzopyran-4-ones **20** (Scheme 4). These photoreactions may be occurring from the primary cleavage of the carbon halogen bond to give α -carbonyl radicals and/or cations. The ionic routes seem to be more favorable in acetonitrile than in hexane. The involvement of radical and ionic pathways in the photochemistry of **18** is also

supported by detection of Br_2^- in the laser flash photolysis experiments.

2.3. Photochemical oxidation

Photochemical reaction of 7-methoxy-3-phenyl-2-[*(E*)-2-(thiophen-2-yl)ethenyl]-4*H*-chromen-4-one **21** has been reported by Miya et al. (2012). The methanolic solution of **21** containing iodine on photolysis in the presence of air afforded 9-methoxy-5-thiophenyl-12*H*-benzo[a]xanthene-12-one **22**, 2-formyl-7-methoxyiso-flavone **23** and thiophene-2-aldehyde **24** (Scheme 5). This reaction provides an easy and greener route for the preparation of xanthones.

2.4. Photochemical ring contraction

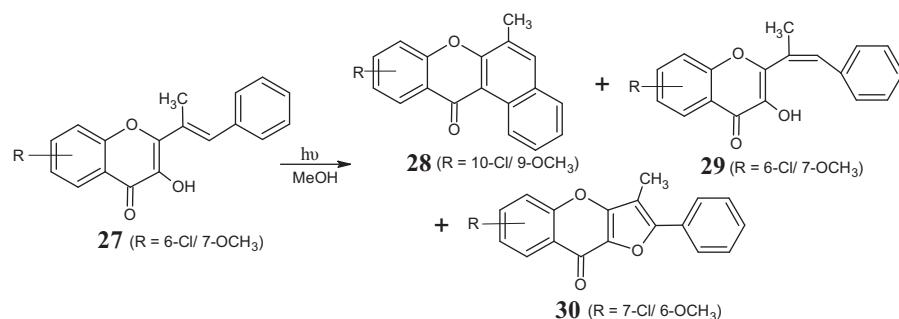
The photolysis (Bala et al., 2007) of 3-hydroxychromone **25** around its λ_{max} (360 nm) yielded the photo ring contracted product 6-chloro-3-hydroxy-3-(2'-thienyl)-1,2-indandione **26** (Scheme 6) which was realized in high yields.

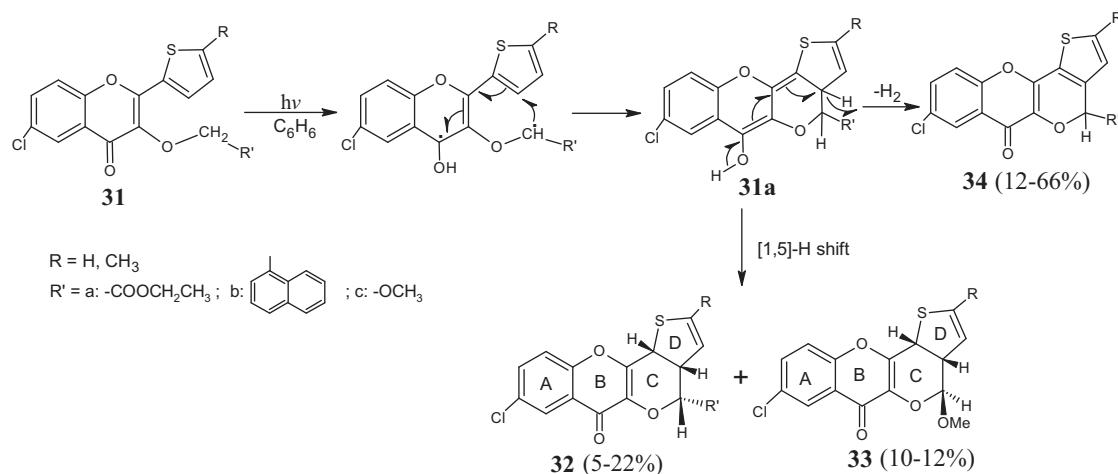
But the photolysis of 2-styryl-3-hydroxychromone (Berar et al., 2008) **27** provides exotic cyclic products through excited state proton transfer (Scheme 7). In these reactions, linear novel tricyclic 9*H*-furo[3,2-*b*]chromen-9-ones **30** (25–26%), angular fused tetracyclic xanthenones **28** (20–22%) and isomerized products **29** (20–35%) are obtained as the major photoproducts.

2.5. Photochemical H-abstraction

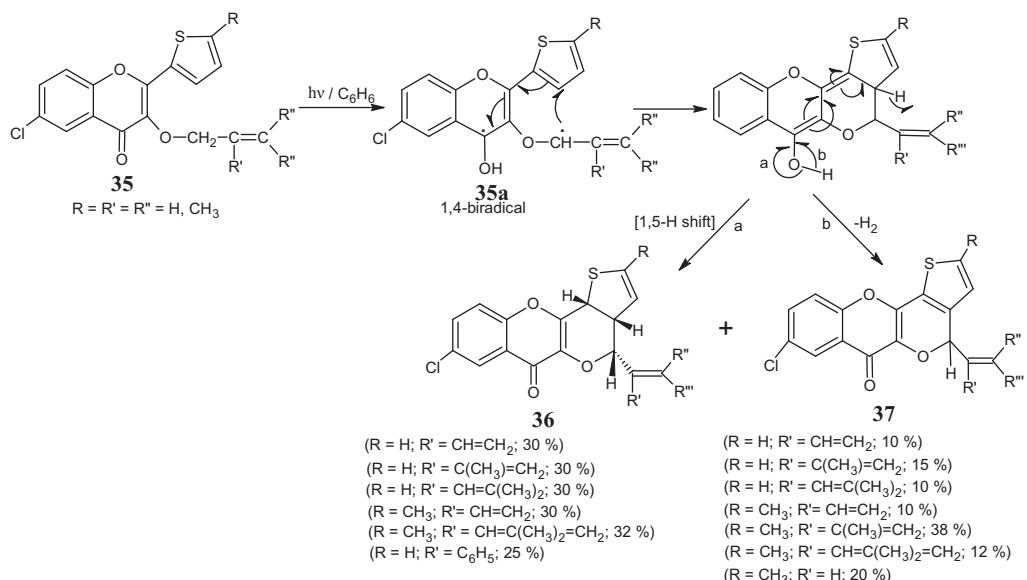
2.5.1. Synthesis of tetracyclic products

We have investigated the photolysis of 3-alkoxychromones (Kumar and Yusuf, 2007; Yusuf et al., 2007) **31** and stereochemical feature of the photoproduct was found to be dependent upon the nature of substituent present at the 3-alkoxygroup of the chromone moiety. These photoreactions

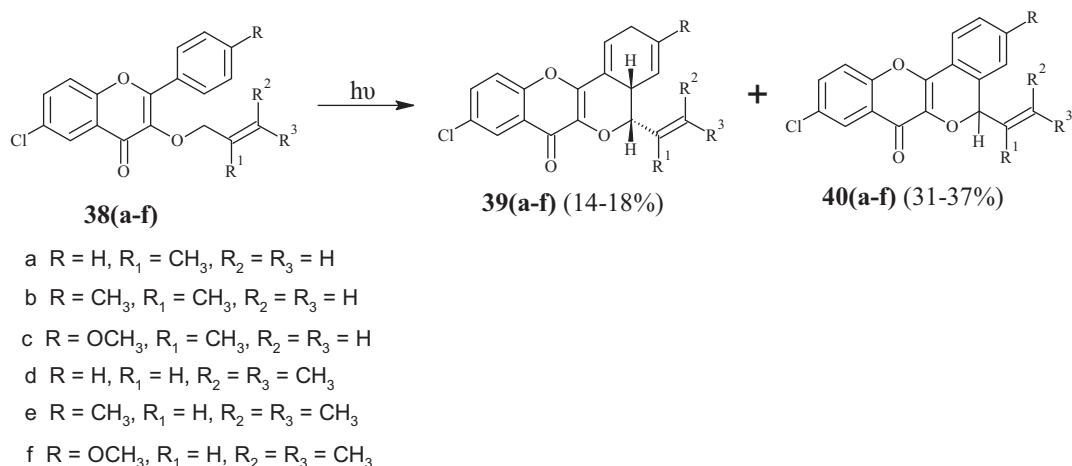
**Scheme 7** Photolysis of 2-styryl chromones.



Scheme 8 Synthesis of tetracyclic products.



Scheme 9 Synthesis of tetracyclic compounds.

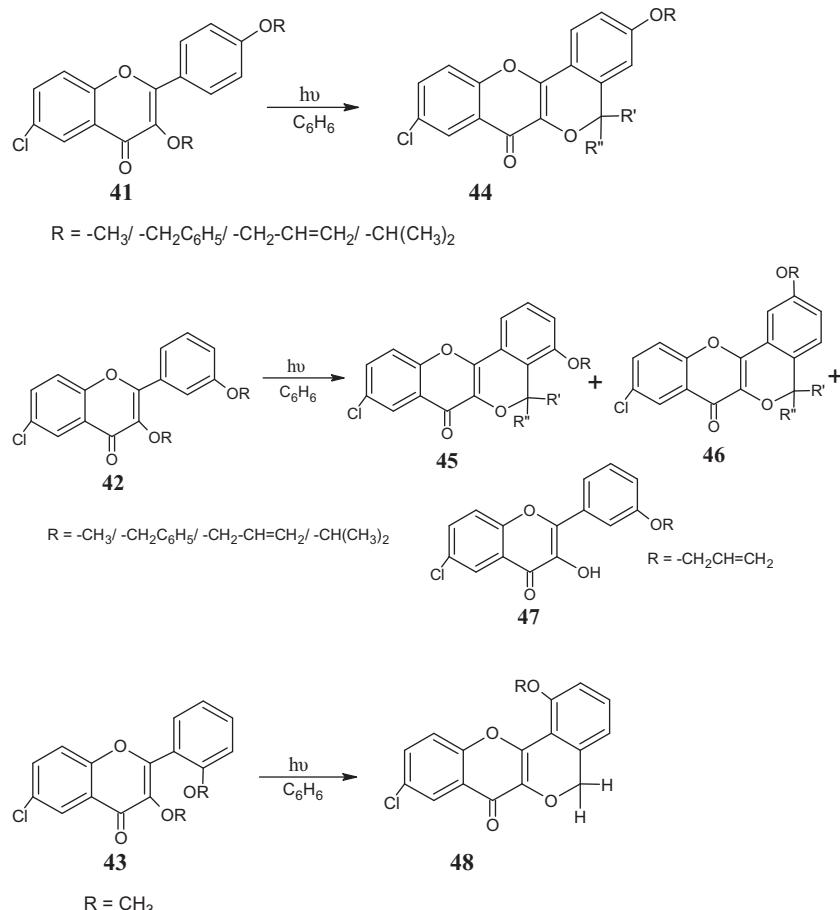


Scheme 10 Synthesis of angular tetracyclic products.

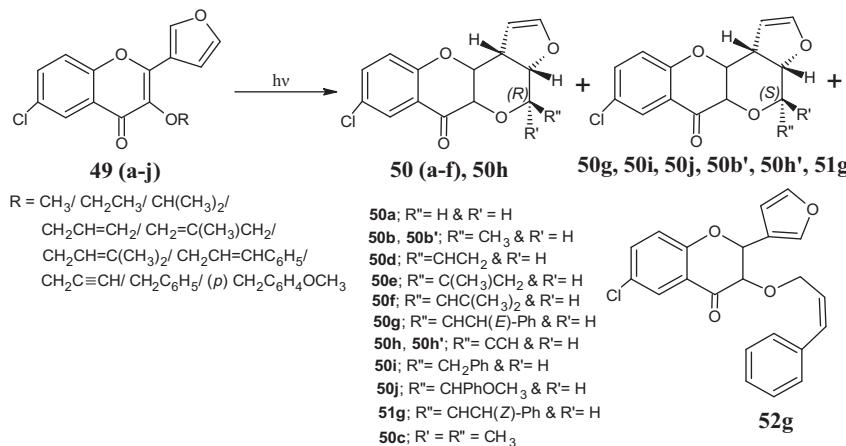
proceed via γ -H abstraction by the photoexcited C=O group from the 3-alkoxy moiety to provide 1,4-biradical which upon cyclization with the 2-aryl ring give **31a**. The latter either undergoes [1,5]-H shift to dihydrocyclized products **32** or suffers the loss of H₂ to generate dehydrogenated cyclized products **34** (**Scheme 8**). It was observed that the methoxy ($-\text{OCH}_3$) substituted dihydrocyclized compound **33** contains the heavier group at the pseudo-axial position on the pyran

ring C to avoid lone pair-lone pair repulsion while such groups prefer the pseudo-equatorial position in the naphthalene and ester substituted derivatives **32**.

The phototransformations of 3-alkoxy-2-thienylchromones (**Yusuf et al., 2008**) **35** also yielded dihydrocyclized **36** and dehydrogenated cyclized products **37** via intermediate 1,4-biradical (**Scheme 9**). These photoreactions presented better chemical efficiency than 3-benzyloxy and 3-methoxy-chro-



Scheme 11 Synthesis of tetracyclic compounds.



Scheme 12 Synthesis of conformational isomers.

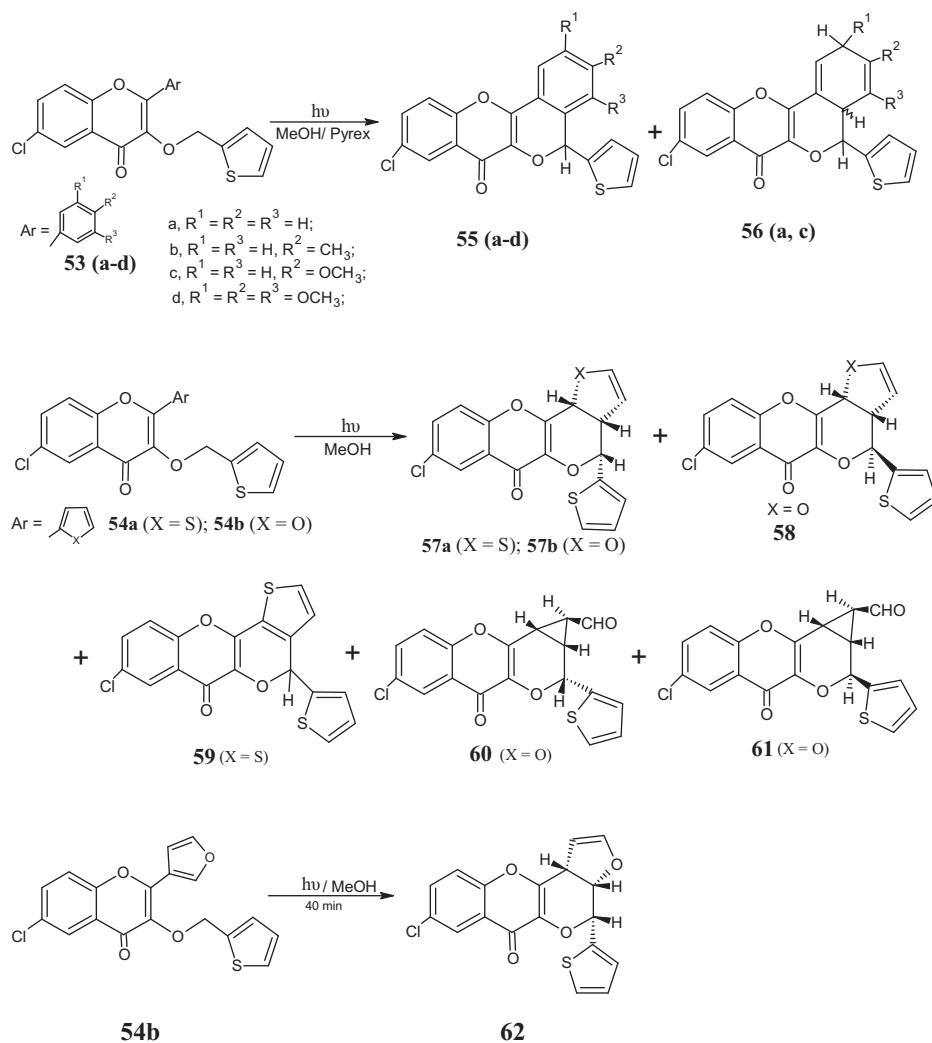
mones (Gupta et al., 1999) which may be explained on the basis of higher stability of allylic free radical **35a** than benzylic and methyl free radicals. Here products are obtained only through the involvement of 1,4-biradical **35a**. In these reactions, dehydrogenated cyclized products **37** are obtained independently from the intermediate 1,4-biradical **35a** and are not the dehydrogenated product of the corresponding dihydro derivatives **36**. This aspect was confirmed from the irradiation of **36** in benzene which did not provide any product similar to **37** rather a polymeric material was always observed.

The photoreorganizations of 3-allyloxy-2-arylchromones (Kumar and Yusuf, 2008) **38(a-f)** provided two types of angular tetracyclic compounds **39(a-f)** and **40(a-f)** (Scheme 10). The greater yields of oxidized products in these photoreactions than their corresponding dihydroderivatives could be explained on the basis of aromaticity and hence greater stability of the dehydrogenated products whereas dihydroderivatives are non aromatic and less stable. These photoreactions present the general method for the preparation of vinyl substituted benzopyronopyrans.

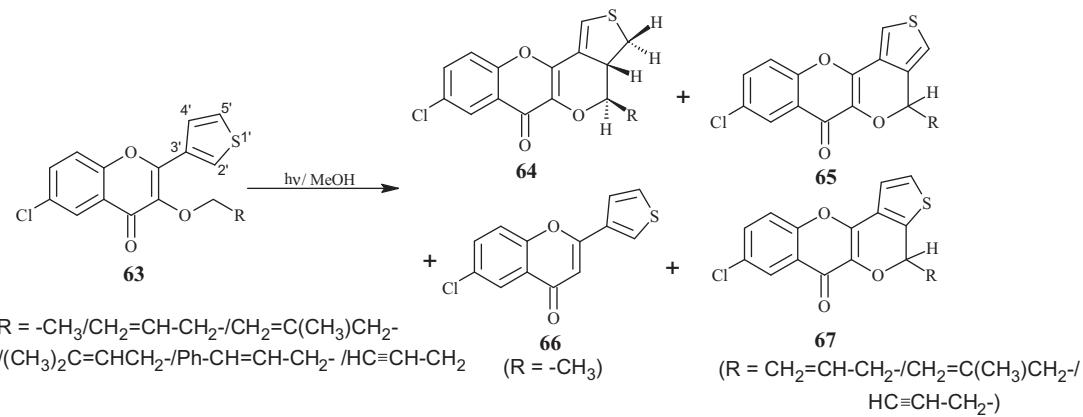
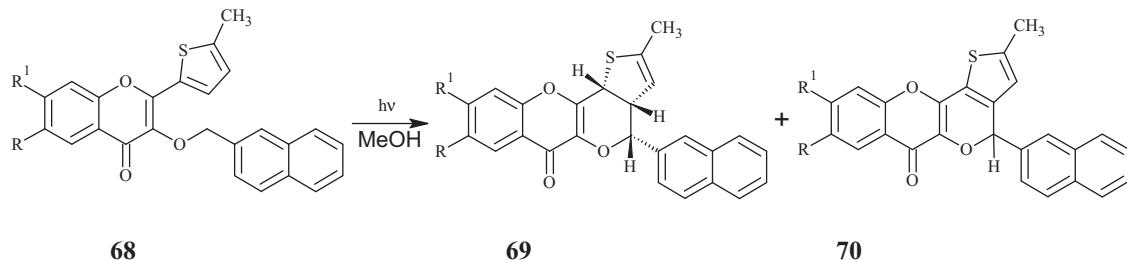
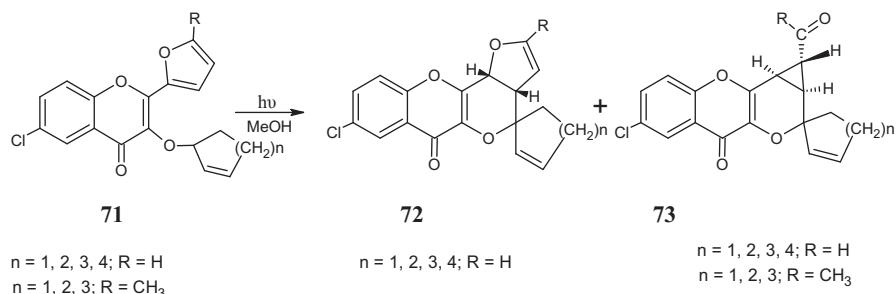
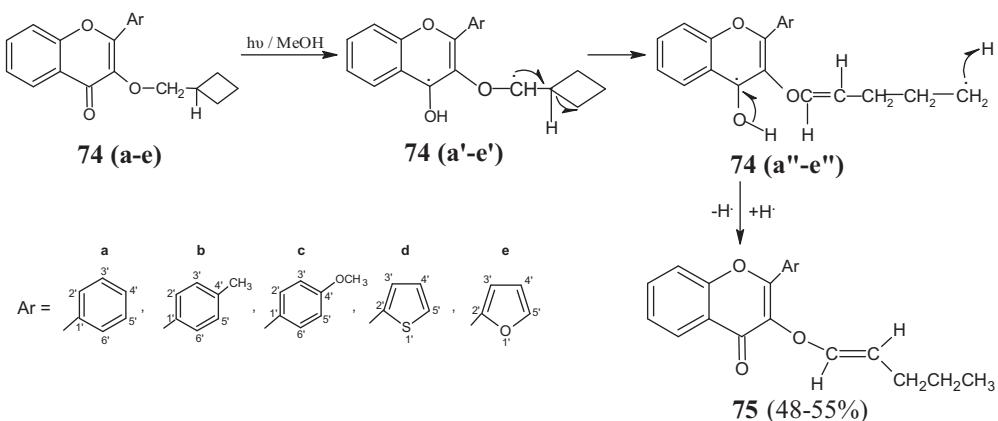
The photoproduct formations in 3-alkoxy-2-(alkoxyphenyl) chromones (Kamboj et al., 2009a,b) **41-43** have been found to be dependent upon the nature of the 2-aryl ring (Scheme 11).

The photolysis of chromone **41** in which the position no. 4 was occupied by the alkoxy group yielded only one product **44** (22–46%), but in compound **42** where the alkoxy group was present at position no. 3, two isomeric products **45** (12.5–26%) and **46** (11–19%) were formed and an additional product **47** (5.5%) was also realized when the substituent was the allyl group. The photoirradiation of chromone bearing the alkoxy group at position no. 2 of the 2-aryl ring did not yield any product even upon prolonged irradiations except in 3-methoxychromone **43** which resulted in the formation of **48** as the cyclized product.

The photocyclization reactions of 3-alkoxy/allyloxy-6-chloro-2-(furan-3-yl)-4H-chromen-4-ones **49(a-j)** have also been investigated (Kamboj et al., 2009a,b) which occur through Norrish type II process to give **50(a-j)** (11–50%), **51g** (10%) and **52g** (25%). The nature of the 3-alkoxy/allyloxy group influenced the photoproduct formations (Scheme 12). The stereochemistry of ring C was the interesting feature of the photoproduct which is present in half chair confirmation. In photoproducts **50(a-j)**, **50b'**, **50h'**, **51g** and **52g**, the stereochemistry of C/D ring junction was *cis* due to minimum energy. In compounds **50a** and **50c**, both confirmations are equivalent because substituents at C-4 were same. The *trans*



Scheme 13 Synthesis of tetracyclic products.

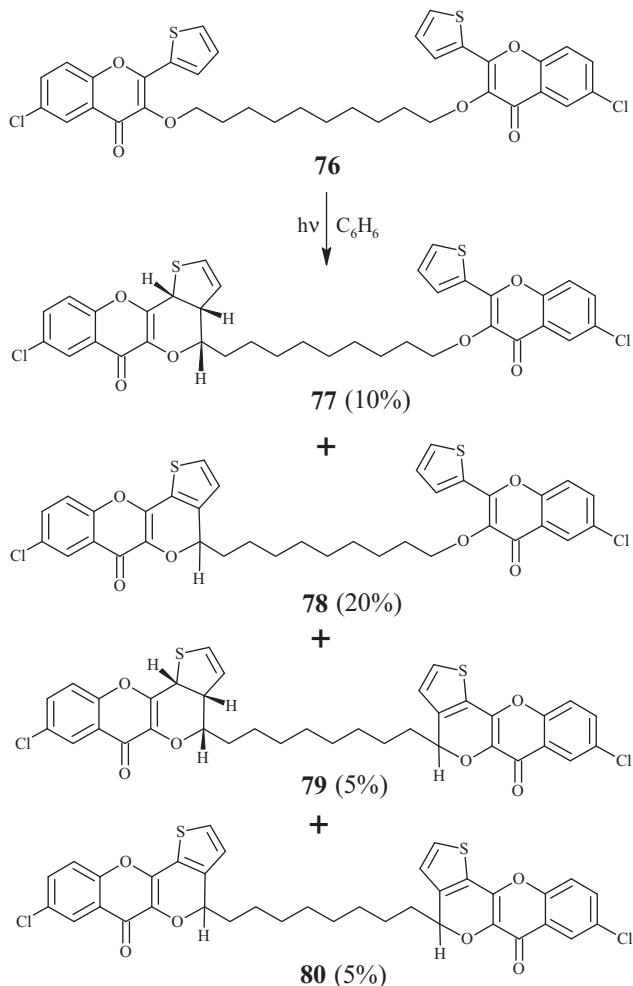
**Scheme 14** Photoirradiation of 3-alkoxy-6-chloro-2-(thiophen-3-yl)-4*H*-chromen-4-ones.**Scheme 15** Synthesis of angular tetracyclic products.**Scheme 16** Synthesis of spiropyrans.**Scheme 17** Synthesis of vinyl ethers.

disposition of H-3a and H-4 in compounds **50b**, **50d–50f** and **50h** and *cis* disposition in **50g**, **50i**, **50j**, **50b'**, **50h'** and **51g** could be explained on the basis of Karplus rule.

Some results (Kamboj et al., 2010) have also been reported upon the photolysis of 2-aryl-6-chloro-3-[(thiophen-2-yl)methoxy]chromones **53(a–d)** and **54(a–b)** in a Pyrex filtered light from a 125 W Hg vapor lamp under nitrogen atmosphere (Scheme 13). The major interest in this study was to investigate the effect of thiophene ring at the 3-alkoxy group upon photo-product formation and also to investigate the possibility of any photo-transposition. These photoreactions afforded many tetracyclic products **55–62** (Scheme 13).

Photoirradiation of 3-alkoxy-6-chloro-2-(thiophen-3-yl)-4H-chromen-4-ones (Kamboj et al., 2011a,b) **63** under the inert atmosphere produced tetracycized products **64–67** (Scheme 14). These reactions were regiospecific in nature as here the products were obtained from the clipping of intermediate 1,4-biradical with C-2' of the thienyl ring to give **67** (20%) while the products **64** (10–35%) and **65** (8–45%) were obtained from the clipping of 1,4-biradical with C-4' of the 2-thienyl ring. Here photodealkylated product **66** (14%) was also obtained.

Similarly, photolysis of methanolic solution of 2-(5-methylthiophen-2-yl)-3-[(naphthalen-2-yl)methoxy]-4H-chromen-4-



Scheme 18 Photocyclization of thienyl bischromones.

ones (Kamboj et al., 2011a,b) **68** yielded angular tetracyclic products **69** (26–42%) and **70** (15%) (Scheme 15).

2.5.2. Synthesis of spiropyrans

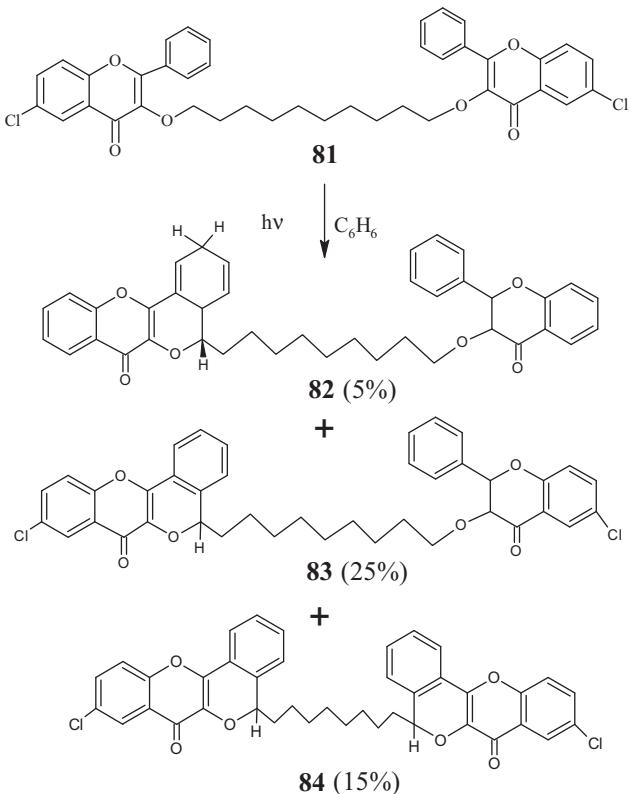
Gupta et al. (2007) have investigated the photolysis of 2-furyl-3-alkenoxybenzopyrans **71** in MeOH which led to the formation of exotic spirocyclic products **72** (10%) and **73** (18–20%) (Scheme 16).

2.5.3. Synthesis of vinyl ethers

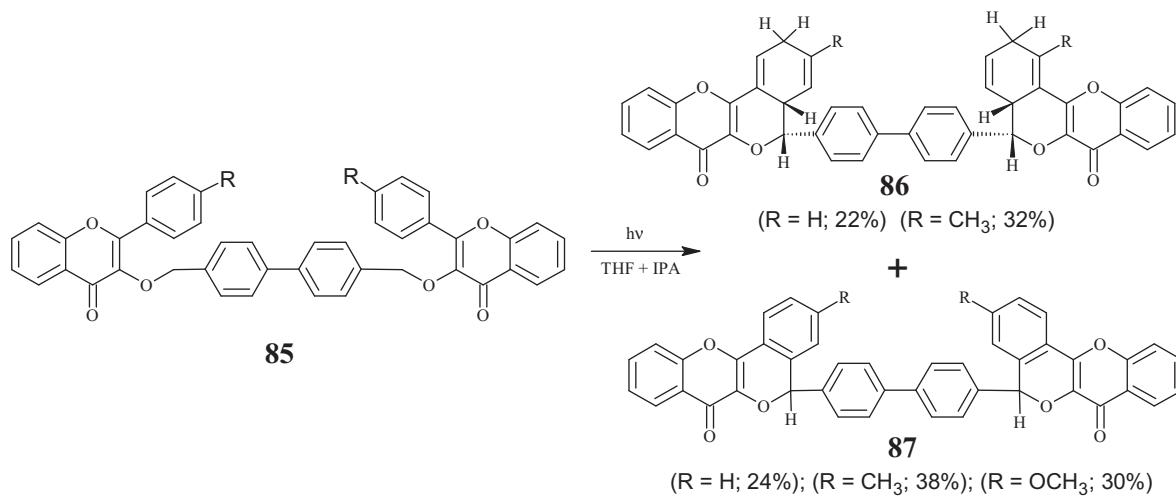
In order to investigate the effect of the ring strain upon the intramolecular H-abstraction, we have studied the photochemical reaction of some 3-cyclobutylmethoxy-2-aryl/thienyl/furan (Yusuf et al., 2017) **74(a–e)**. These chromones were photoirradiated in MeOH in a Pyrex reactor under N₂ atmosphere and column chromatographic work up of photolysates provided vinyl ethers **75(a–e)** (Scheme 17) in good yields. These photoreactions occurred via γ H-abstraction to give 1,4-biradical **74(a'–e')** which further led to the cleavage of the cyclobutyl ring due to its inherent ring strain to give 1,8-biradical **74(a''–e'')**. The latter finally captured H[•] from the solvent (MeOH) to provide vinyl ethers **75(a–e)** as the end products (Scheme 17). The significance of this method lies in the fact that here vinyl ethers are obtained under the mild conditions without using any toxic and specific reagents.

3. Photochemical H-abstraction in bischromones

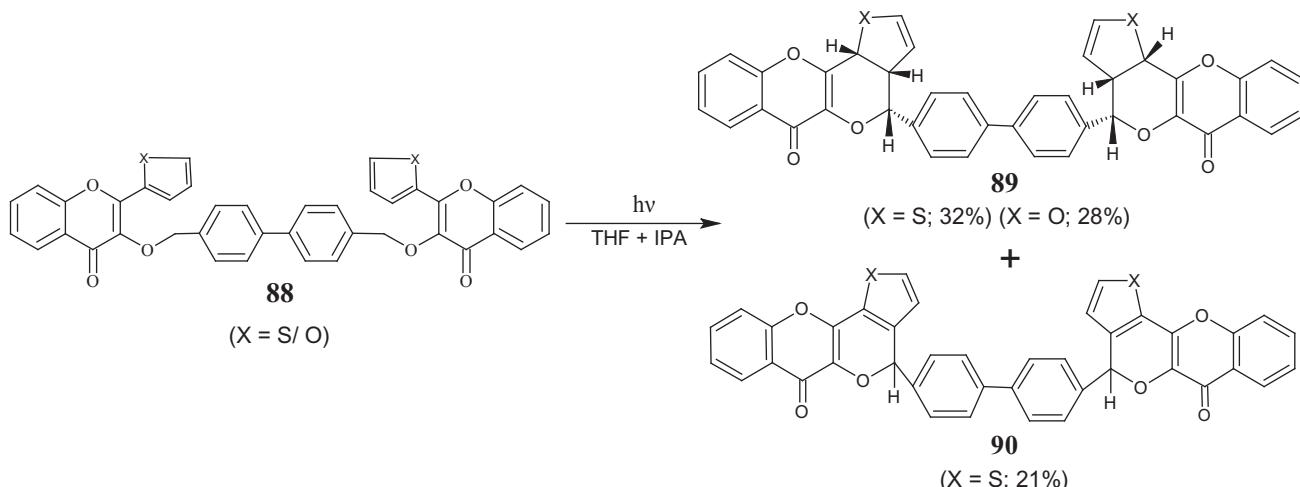
Bischromones are the molecules in which two chromone moieties are linked together through a carbon chain of varying length or geometry. Photoirradiations of these molecules lead



Scheme 19 Photocyclization reactions.



Scheme 20 Photochemical reaction of biphenyl based bischromones.



Scheme 21 Photolysis of biphenyl based bischromones.

to the formation of photoproducts from the involvement of one chromone as well as both chromone moieties. The nature of internal chain was found to be affecting the course of these reactions.

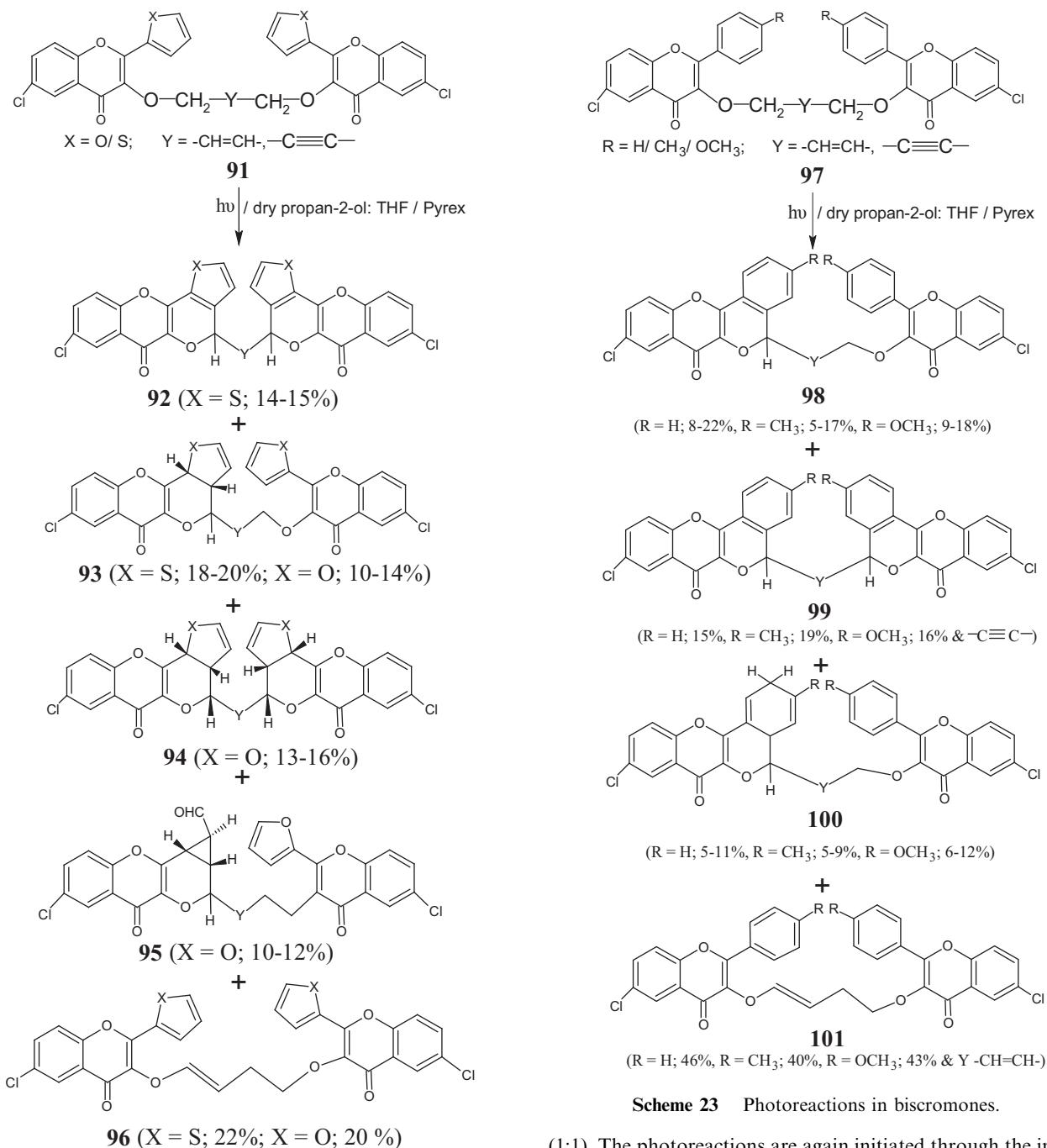
3.1. Photocyclization reaction

To study the effect of lengthy internal chain, we have attempted the photocyclizations of bischromones (Yusuf et al., 2006) **76** and **81** built around decyl chain (Schemes 18 and 19). These reactions are also occurring through intramolecular H-abstractions involving 1,4-biradicals which usually undergo cyclization with the 2-thienyl/phenyl ring to give dihydrocylized (**77**, **79** and **82**) and dehydrocylized compounds (**78**, **80**, **83** and **84**). The photoproducts **77**, **78**, **82** and **83** could be available from the reaction of one chromophore only while both chromone moieties reacted efficiently to provide **79**, **80** and **84**. The photolysis of bischromones built around decyl chain resulted in better chemical efficiency in terms of photoproduct formation and distribution, in comparison to bischromones built around propyl/butyl/pentyl chain (Gupta et al.,

2002). Introduction of the lengthy intermediate bridge (decyl moiety) in bischromone **76** and **81** has been instrumental in furnishing total photolytic conversion to an extent about one and half times greater than for bischromones built around shorter length (Gupta et al., 2002) (propyl/butyl/pentyl). Probably, this phenomenon could be ascribed to the ease of formation of the excited state intramolecular complexes in the bischromones with shorter spacers. Thus, as the distance increases between the chromophores, the probability of intramolecular complex formation decreases, minimizing the involvement of deactivation processes that cause the improved yields and distributions of photoproducts.

Here, the length of the extended spacer unit has been found to be affecting the yield and distribution of the photoproducts and polarity of the solvent did not show any significant effect on the product formation.

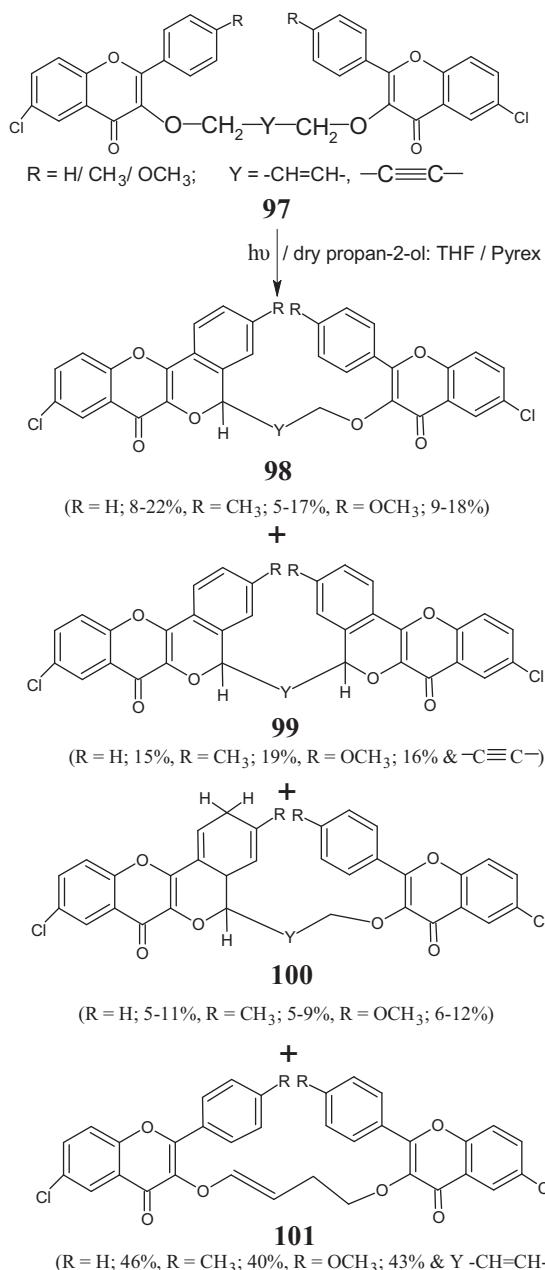
We have also recently reported the photochemical reaction of some biphenyl based bischromen-4-ones (Yusuf et al., 2012) **85** and **88** under inert atmosphere using dry isopropyl alcohol and THF (1:1) as the solvent system (Schemes 20 and 21). The chromatographic separation of the photolysates yielded

**Scheme 22** Photoisomerization in bischromones.

various hydrogenated cyclized **86** and **89** and dehydrogenated cyclized **87** and **90** products in moderate yields. This study provides the photochemical method for the preparation of new diisochromenochromen-4-one linked through the biphenyl moiety.

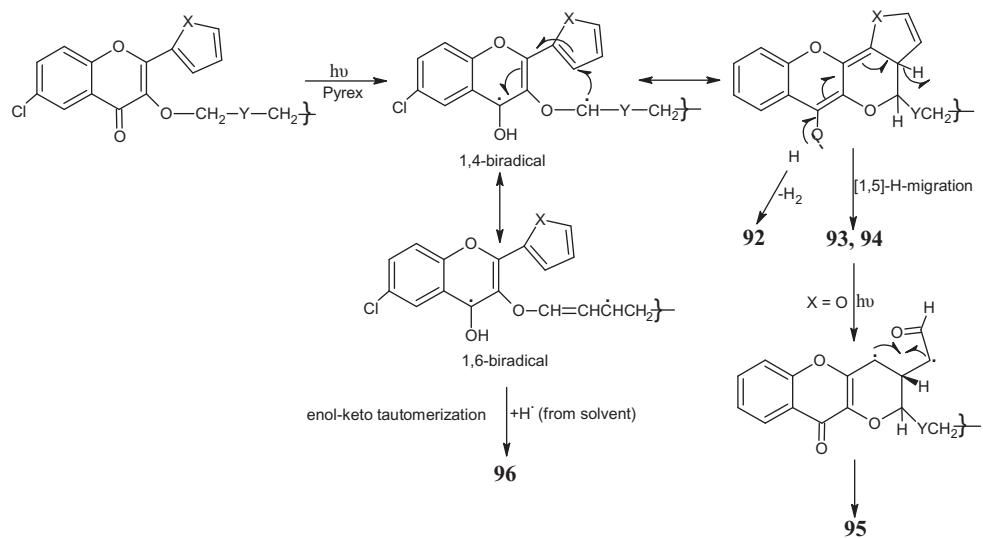
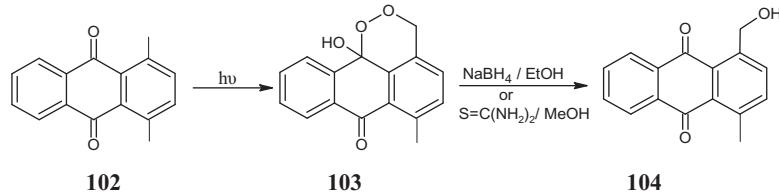
3.2. Photoisomerization

In order to investigate the effect of solvent polarity upon the photoproduct formation, we have carried out the photolysis of 2-thienyl/furyl-3-but enyl/butynyl-bischromones (Kumar and Yusuf, 2010) **91** (Scheme 22) in dry propan-2-ol:THF

**Scheme 23** Photoreactions in biscromones.

(1:1). The photoreactions are again initiated through the intramolecular H-abstraction that led to the formation of vinyl bischromones **96** along with the ring contracted **95**, normal hydrogenated cyclized **93** and **94** and dehydrogenated cyclized **92** photoproducts. When the photoreactions were carried out in dry benzene, only cyclized products were isolated and no product similar to vinyl ethers **96** was observed. Similarly, 2-phenyl/tolyl/anisyl-3-but enyl/butynyl-bischromones (Kumar and Yusuf, 2009) **95** also generated four types of new photoproducts **96-98** (Scheme 23). The photochemical transformation of these bischromones was found to be dependent upon the nature of the 2-aryl ring and H-donating capability of the solvent.

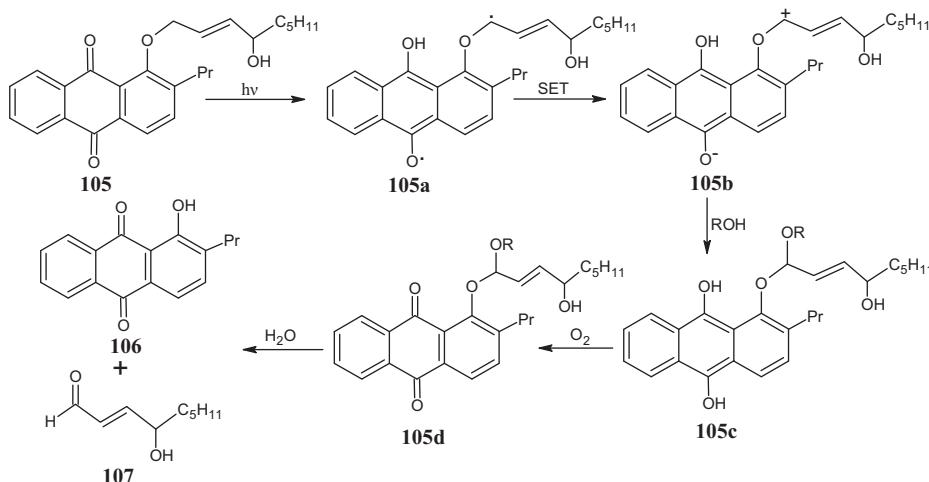
The results presented in above schemes (Schemes 22 and 23) may be explained by considering the isomerization of intermediate 1,4-biradical to 1,6-biradical that further captures hydro-

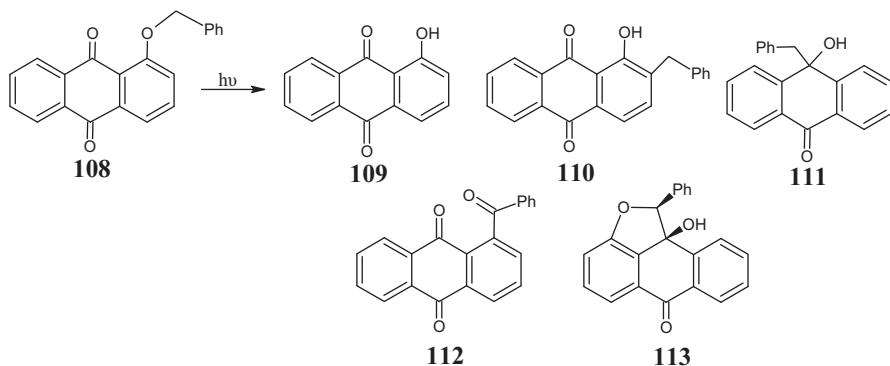
**Scheme 24** Mechanism of photoreaction.**Scheme 25** Photo-oxidation in anthraquinone.

gen from the solvent molecule (propan-2-ol) and subsequently undergoes keto-enol tautomerization reaction to give **96**. But, the initially formed 1,4-biradical in 2-butyne-bischromone is reluctant to provide 1,6-biradical, because such an isomerization would have yielded an unstable allenic ether. Thus, in these bischromones major photoproducts are obtained through the cyclization of 1,4-biradical under the polar protic and nonpolar aprotic conditions (**Scheme 24**) whereas isomerized product is only realized under the polar protic medium (THF + IPA).

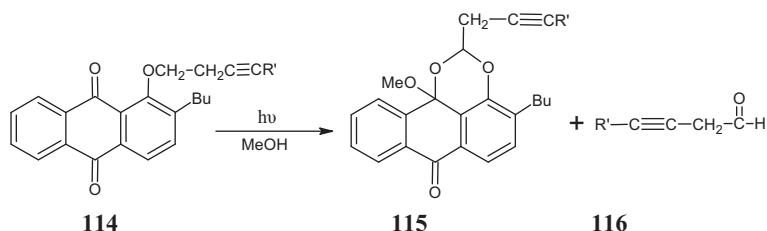
4. Photochemical reactions of anthraquinones

Anthraquinones are another category of important and well studied (Lukeman et al., 2002; Yoshihara et al., 2001; Huang et al., 2007; Perumal et al., 2009; Langhals and Saulich, 2002; Gorner, 2003; Zhu et al., 2005; Ren et al., 2009; Maurino et al., 2008; Gouloumis et al., 2006; Qureshi et al., 2011) organic compounds and absorb UV light resulting in intersystem crossing and also act as electron and hydrogen atom acceptor.

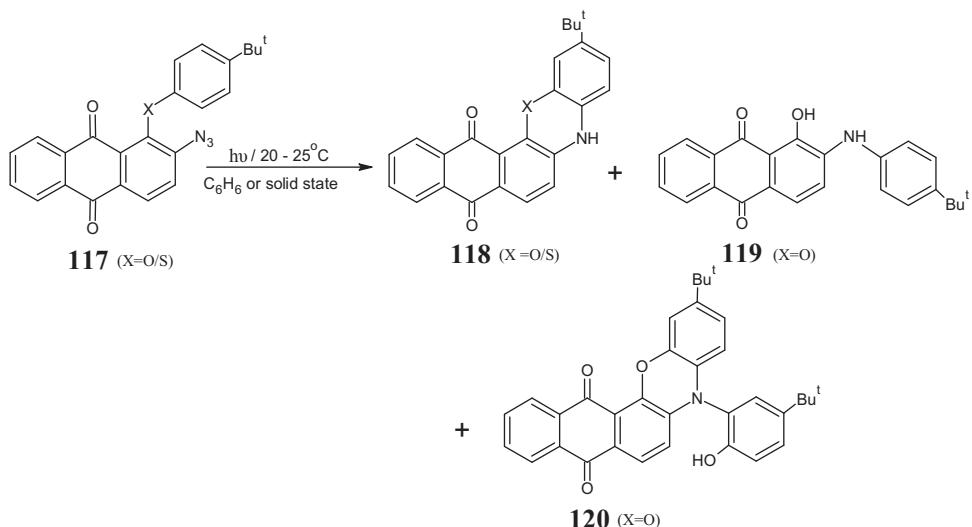
**Scheme 26** Synthesis of α , β -unsaturated aldehyde.



Scheme 27 Synthesis of 1-hydroxy-9,10-anthraquinones.



Scheme 28 Synthesis of 3-alkynals.



Scheme 29 Photochemical cyclization in anthraquinone derivatives.

4.1. Photo-oxidation

The photolysis of 1,4-dimethyl-9,10-anthaquinones **102** was carried out by Elkaza and Jones (2010) in the presence of O₂ that yielded endoperoxide **103** and the reduction of later with NaBH₄ provided 4-methyl-1-hydroxymethyl-9,10-anthaquinones **104** as the final product (Scheme 25).

4.2. Photochemical H-abstraction

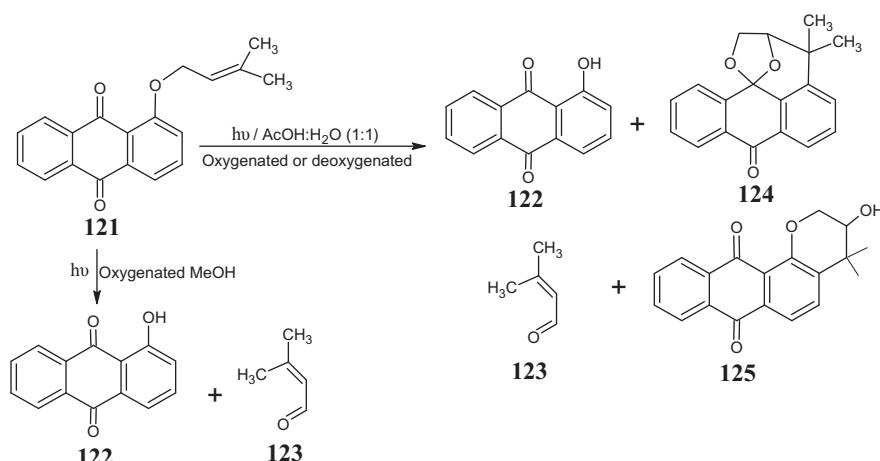
4.2.1. Synthesis of α,β -unsaturated aldehyde

(E)-1-(4-Hydroxynon-2-enyloxy)-2-propylanthracene-9,10-dione **105** upon photolysis (Brinson and Jones, 2004) suffers

H-abstraction followed by single electron transfer and then trapped by the solvent followed by oxidation to generate 1-hydroxyanthraquinone **106** and 4-hydroxy-2-nonenal **107** as the photoproducts (**Scheme 26**).

4.2.2. Synthesis of 1-hydroxy-9,10-anthraquinones

Photochemistry of 1-benzyloxy-9,10-anthraquinones **108** was described by [Sharma and Jones \(2010\)](#). This compound also undergoes intramolecular δ H-abstraction which further leads to the oxidative cleavage of the 1-alkoxy group as an aldehyde ([Blankespoor et al., 1991, 1995, 2002; Smart et al., 1997](#)). In this photoreaction, five types of photoproducts **109–113** are obtained ([Scheme 27](#)).



Scheme 30 Photolysis of 1-(3,3-dimethyl-2-proenyl)-9,10-anthraquinones.

4.2.3. Synthesis of 3-alkynals

Photolysis of 1-(3-alkynoxy)-9,10-anthraquinone ([Blankespoor et al., 2009](#)) **114** in deoxygenated methanol yielded diacetals **115** and 3-alkynals **116** ([Scheme 28](#)) as the major photoproducts.

4.3. Photochemical cyclization

The photochemical reaction of 1-aryloxy-2-azido-9,10-anthraquinone **117** both in solid state (Klimenko et al., 2006) and solution phase has been studied (Klimenko et al., 2002, 2003, 2001). In the solution phase, three photoproducts **118–120** were obtained while **118** and **120** were realized from the photolysis in solid state (Scheme 29).

The photolysis of 1-(3,3-dimethyl-2-proenoxy)-9,10-anthraquinone (Brinson et al., 2005) **121** in oxygenated and deoxygenated water and acetic acid medium (1:1) led to the generation of photodealkylated (**122**), aldehyde (**123**) and photocyclized **124** and **125** products (Scheme 30).

4.4. Laser flash photolysis

Laser flash photolysis and external field have also been used to study the interaction of 9,10-anthraquinones (AQ) and 2-methyl-1,4-naphthoquinone (MQ) with uracil (U), 1,3-dimethyluracil (dmU) and uridine (dU) in homogenous organic and heterogeneous micellar media ([Bose and Basu, 2008](#)) in order to investigate the effect of media on molecules and any change in reactivity on account of substitution. Both quinones behaved similarly in homogeneous bases. Uracil (U) has undergone electron transfer (ET) and hydrogen (H) transfer whereas dU and dmU have failed to exhibit any ET. However in SDS micelles, Hydrogen (H) transfer dominated over electron transfer (ET) in both quinones with U. AQ showed difference in the extent of H abstraction with bases in SDS. With U and dU, H abstraction resulted in the formation of AQH^+ while dmU has produced both AQH^+ and AQH_2 , the latter being formed by two successive H abstraction.

5. Conclusion

Photochemistry of alkoxy substituted chromones, bischromones and anthraquinones is an important source of many

exotic heterocyclic products which are not accessible through normal thermal routes. Photoirradiation of chromones leads to the formation of dimer and oxametathetic products through intermolecular and intramolecular dimerization, respectively. Chromones also undergo photodehalogenation and photooxidation. The photocyclization reaction of 3-alkoxychromone provides many interesting heterocyclic compounds like benzopyronopyrans, spiropyrans and vinyl ether derivatives through intramolecular H-abstraction reactions. The nature of the 2-aryl ring, 3-alkoxy group and polarity of the solvents are found to affect the formation and stereochemistry of the final photoproducts. Bischromones also undergo easy photocyclization and photoismerization and here major products are obtained through 1,4-biradical under polar protic as well as aprotic conditions. Anthraquinone derivatives also yield many useful compounds through photo-oxidation, photochemical H-abstraction and laser flash photolytic conditions. Thus, these photoreactions present themselves an important tool for the synthesis of many exotic five and six membered oxygen containing heterocyclic compounds. These products are realized under the normal conditions without using any expansive and toxic reagent which describes the synthetic utility of these methodologies.

Acknowledgement

Authors are highly thankful to CSIR, New Delhi, India for providing the financial support (CSIR-SRF).

References

Bala, R., Kumar, R., Yusuf, M., Bansal, W.R., 2007. Indian J. Chem. A 46, 1440.

Berar, S., Berar, U., Gupta, S.C., Kamboj, R.C., 2008. Chin. Chem. Lett. 19, 780.

Blankespoor, R.L., De Jong, R.L., Dykstra, R., Hamstra, D.A., Rozema, D.B., VanMeurs, D.P., Vink, P., 1991. J. Am. Chem. Soc. 113, 3507.

Blankespoor, R.L., Smart, R.P., Batts, E.D., Kiste, A.A., Lew, R.E., Van der Vliet, M.E., 1995. J. Org. Chem. 60, 6852.

Blankespoor, R.L., DeVries, T., Hansen, E., Kallemeyn, J.M., Klooster, A.M., Mulder, J.A., Smart, R.P., Vander Griend, D.A., 2002. J. Org. Chem. 67, 2677.

Blankespoor, R.L., Boldenow, P.J., Hansen, E.C., Kallemeyn, J.M., Lohse, A.G., Rubush, D.M., Vrieze, D.J., 2009. Org. Chem. 74 (10), 3933.

Bose, A., Basu, S., 2008. *J. Phys. Chem. A* 112 (47), 12045. <http://dx.doi.org/10.1021/jp805632>.

Boyd, M.K., Zopp, G.K., 2004. *Annu. Rep. Prog. Chem. B* 100, 351.

Brinson, R.G., Jones, P.B., 2004. *Org. Lett.* 6 (21), 3767.

Brinson, R.G., Hubbard, S.C., Zuidema, D.R., Jones, P.B., 2005. *J. Photochem. Photobiol. A: Chem.* 175, 118.

Chapman, O.L., Weiss, D.S., 1973. *Org. Photochem.* 3, 197.

Coxon, J.M., Halton, B., 1987. *Organic Photochemistry*, second ed. Cambridge University Press, Cambridge.

Coyle, J.D., 1985. *Tetrahedron* 41, 5393.

Coyle, J.D., Carless, H.A.J., 1972. *Chem. Soc. Rev.* 1, 465.

De Leeuw, J., Assen, Y.J., Van der Beek, N., Bjerring, P., Neumann, H.A.M., 2011. *J. Eur. Acad. Dermatol. Venereol.* 25, 74.

Delgado, J., Espinós, A., Jiménez, M.C., Miranda, M.A., 2007. *ARKIVOC VIII*, 224.

Deshmukh, S.K., Mishra, P.D., Kulkarni-Almeida, A., Verekar, S., Sahoo, M.R., Periyasamy, G., Goswami, H., Khanna, A., Balakrishnan, A., Vishwakarma, R., 2009. *Chem. Biodivers.* 6 (5), 784.

Edwards, A.M., Howell, J.B.L., 2000. *Clin. Exp. Allergy* 30, 756.

Eichler, J., Herz, C.P., Naito, I., Schnabel, W., 1980a. *J. Photochem.* 12, 225.

Eichler, J., Herz, C.P., Schnabel, W., 1980b. *Angew. Makromol. Chem.* 91, 39.

Elkaza, S., Jones, P.B., 2010. *J. Org. Chem.* 75, 412.

Frick, R.W., 2000. *Angiology* 51, 197.

Gamal-Eldeen, A.M., Djemgou, P.C., Tchuendem, M., Ngadjui, B.T., Tane, P., Toshifumi, H., 2007. *Z Naturforsch C* 62 (5-6), 331.

Gomes, A., Neuwirth, O., Freitas, M., Couto, D., Ribeiro, D., Figueiredo, A.G., Silva, A.M., Seixas, R.S., Pinto, D.C., Tomé, A.C., Cavaleiro, J.A., Fernandes, E., Lima, J.L., 2009. *Bioorg. Med. Chem.* 17 (20), 7218.

Gorner, H., 2003. *Photochem. Photobiol.* 77, 171.

Gouloumis, A., Gonzalez-Rodriguez, D., Vazquez, P., Torres, T., Liu, S., Echegoyen, L., Ramey, J., Hug, G.L., Guldi, D.M., 2006. *J. Am. Chem. Soc.* 128, 12674.

Gupta, S.C., Sharma, S., Saini, A., Dhawan, S.N., 1999. *J. Chem. Soc. Perkin Trans. I*, 2391.

Gupta, S.C., Yusuf, M., Arora, S., Sharma, S., Kamboj, R.C., Dhawan, S.N., 2002. *Tetrahedron* 58, 3095.

Gupta, S.C., Thakur, M., Sharma, S., Berar, U., Berar, S., Kamboj, R.C., 2007. *Beilstein J. Org. Chem.* 3, 14.

Hajhashemi, V., Ghannadi, A., Heidari, A.H., 2012. *Res. Pharm. Sci.* 7 (2), 73.

Hoffmann, N., 2008. *Chem. Rev.* 108, 1052.

Holgate, S.T., Polosao, R., 2008. *Nat. Rev. Immunol.* 8, 218.

Horspool, W.M., Song, P.S., 1995. *CRC Hand Book of Organic Photochemistry & Photobiology*, first ed. CRC Press.

Horvat, M., Millinaric-Majerski, K., Basaric, N., 2010. *Croat. Chem. Acta* 83 (2), 179.

Huang, Q., Lu, G., Shen, H.M., Chung, M.C., Ong, C.N., 2007. *Med. Res. Rev.* 27 (5), 609.

Jockusch, S., Landis, M.S., Freiermuth, B., Turro, N.J., 2001. *Macromolecules* 34, 1619.

Kamboj, R.C., Berar, U., Berar, S., Thakur, M., Gupta, S.C., 2009a. *Indian. J. Chem. B* 48, 685.

Kamboj, R.C., Berar, U., Berar, S., Thakur, M., Arora, R., Gupta, S.C., 2009b. *Canadian J. Chem.* 87 (2), 422.

Kamboj, R.C., Berar, U., Berar, S., Siddiqui, Z.N., Gupta, S.C., 2010. *J. Braz. Chem. Soc.* 21 (2), 270.

Kamboj, R.C., Arora, R., Kumar, D., Sharma, G., 2011a. *J. Photochem. Photobiol. A: Chem.* 220, 124.

Kamboj, R.C., Kumar, D., Sharma, G., Arora, R., 2011b. *Chin. J. Chem.* 29, 745.

Khadem, S., Marles, R.J., 2012. *Molecules* 17, 191. <http://dx.doi.org/10.3390/molecules17010191>.

Klimenko, L.S., Pritchina, E.A., Gristan, N.P., 2001. *Russ. Chem. Bull. Int. Ed.* 50, 678.

Klimenko, L.S., Kusov, S.Z., Vlasov, V.M., 2002. *Mendeleev Commun.*, 102.

Klimenko, L.S., Pritchina, E.A., Gristan, N.P., 2003. *Chem. Eur. J.* 9, 1639.

Klimenko, L.S., Kusov, S.Z., Tchabueva, E.N., Boldyrev, V.V., 2006. *Mendeleev Commun.* 16 (4), 224.

Kumar, R., Yusuf, M., 2006. *ARKIVOC IX*, 239.

Kumar, R., Yusuf, M., 2007. *ARKIVOC XVI*, 227.

Kumar, R., Yusuf, M., 2008. *Org. Commun.* 1 (3), 39.

Kumar, R., Yusuf, M., 2009. *Org. Commun.* 2 (1), 7.

Kumar, R., Yusuf, M., 2010. *Indian J. Chem. B* 49, 216.

Langhals, H., Saulich, S., 2002. *Chem. Eur. J.* 8, 5630.

Lemos, L.M., Martins, T.B., Tanajura, G.H., Gazoni, V.F., Bonaldo, J., Strada, C.L., Silva, M.G., Dall'oglio, E.L., de Sousa Júnior, P.T., Martins, D.T., 2012. *J. Ethnopharmacol.* <http://dx.doi.org/10.1016/j.jep.2012.03.006>, Epub 2012 March 15.

Lukeman, M., Xu, M., Wan, P., 2002. *Chem. Commun.*, 136.

Margaretha, P., 1982. *Preparative Organic Photochemistry, Topics in Current Chemistry*. Springer-Verlag, p. 103.

Maurino, V., Borghesi, D., Vione, D., Minero, C., 2008. *Photochem. Photobiol. Sci.* 7, 321.

Michl, J., Koutecký, V.B., 1990. *Electronic Aspects of Organic Photochemistry*. Wiley InterScience, New York.

Miya, M.B., Rao, Y.J., Krupadanam, G.L.D., 2012. *Indian J. Chem. B* 51, 895.

Neckers, D.C., 2008. *Annu. Rep. Prog. Chem. B*, 104, 349.

Nordlund, J.J., 2006. *The pigmentary system: physiology and pathophysiology*, second ed. Blackwell Publishing Inc, Malden, Massachusetts, USA.

Perumal, K., Stalin, V., Chandrasekarenthiran, S., Sumathi, E., Saravanan, A., 2009. *Textile Res. J.* 79 (13), 1178.

Phosrithong, N., Samee, W., Nunthanavanit, P., Ungwitayatorn, J., 2012. *Chem. Biol. Drug Design* 79 (86), 981.

Pitts, J., Wan, J., 1966. *The Chemistry of Carbonyl Compounds*. In: Patai (Ed.). Wiley and Sons, New York, London, p. 823.

Quereshi, S., Khan, A.A., Pandey, A.K., 2011. *Khim. Prir. Soedin.* 47 (4), 465.

Ren, M.G., Bi, N.M., Mao, M., Song, Q.H., 2009. *J. Photochem. Photobiol. A: Chem.* 204, 13.

Ruffmann, R., 1988. *J. Int. Med. Res.* 16, 317.

Sakamoto, M., Kanehiro, M., Mino, T., Fujita, T., 2009. *Chem. Commun.* 19, 2379. <http://dx.doi.org/10.1039/B822829A>.

Sakamoto, M., Yagishita, F., Kanehiro, M., Kasashima, M., Mino, T., Fujita, T., 2010. *Org. Lett.* 12 (20), 4435.

Scaiano, J.C., Johnston, L.J., 1989. *Org. Photochem.* 10, 309.

Shanthi, V., Ramesh, M., Srimai, V., Srinivas, P., Parthasarathy, T., 2013. *Mod. Chem.* 1 (1), 8.

Sharma, S.J., Jones, P.B., 2010. *J. Org. Chem.* 75 (11), 3806.

Sharma, S.K., Kumar, S., Chand, K., Kathuria, A., Gupta, A., Jain, R., 2011. *Curr. Med. Chem.* 18 (25), 3825.

Sisa, M., Bonnet, S.L., Ferreira, D., Westhuizen, J.H.V., 2010. *Molecules* 15, 5196. <http://dx.doi.org/10.3390/molecules15085196>.

Smart, R.P., Peelen, T.J., Blankespoor, R.L., Ward, D.L., 1997. *J. Am. Chem. Soc.* 119, 461.

Valiulin, R.A., Kutateladze, A.G., 2010. *Tetrahedron Lett.* 51 (29), 3803.

Weiss, R.B., 2010. *Semin. Oncol.* 19, 670.

Yang, N.C., Yang, D.H., 1958. *J. Am. Chem. Soc.* 80, 2913.

Yoshihara, T., Yamaji, M., Itoh, T., Nishimura, J., Shizuka, H., Tobita, S., 2001. *J. Photochem. Photobiol. A: Chem.* 140, 7.

Yusuf, M., Kumar, R., Gupta, S.C., 2006. *ARKIVOC XV*, 28.

Yusuf, M., Kumar, R., Bansal, W.R., Bala, R., 2007. *Indian J. Chem. B* 46, 1860.

Yusuf, M., Kumar, R., Gupta, S.C., 2008. *J. Heterocycl. Chem.* 45, 963.

Yusuf, M., Solanki, I., Jain, P., 2012. *Sci. World J. Article ID 954934*.

Yusuf, M., Solanki, I., Jain, P., 2017. *Arab. J. Chem.* 10, S971–S977.

Zhu, L., Khairutdinov, R.F., Cape, J.L., Hurst, J.K., 2005. *J. Am. Chem. Soc.* 128, 825.